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CLAIMS

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[Claim(s)]

[Claim 1] Antibacterial, the polyester resin constituent for fungus-resistance powder coatings which are characterized by making the zeolite particle which made the metal ion chosen as the polyester resin for powder coatings whose limiting viscosity is 0.15 - 0.40 dl/g from silver, copper, and zinc support contain 0.01 to 10% of the weight.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the polyester resin constituent for powder coatings excellent in antibacterial and the fungus resistance.

[0002]

[Description of the Prior Art] In recent years, at a residence, a hospital and works, especially a chemical and food works, the problem by mold propagation in a paint front face etc. has arisen, and the solvent type paint which added antibacterial and the antifungal agent has appeared. However, the environmental pollution by the organic solvent etc. also poses a big problem, and a water paint and a high-solid paint have come to be used in recent years. Then, although the paint which added antibacterial and the antifungal agent to the water paint is proposed, although it is small quantity, since these water paints and a high-solid paint need the organic solvent, they are not desirable on environmental pollution.

[0003] On the other hand, as compared with the conventional solvent type paint, advantages, like it is possible that it is a pollution-free paint, that use can be presented also immediately after paint, that multilayer two coats is unnecessary, a comparatively cheap thing, and to carry out recovery use of the part for the surplus at the time of paint are accepted, and need has expanded powder coatings quickly in recent years as a paint for a protection ornament of members, such as building materials, home electronics, and autparts.

[0004] as a paint which has antibacterial and a fungus resistance, the resin constituent for antibacterial powder coatings which consists of a specific phosphoric-acid zirconium salt and the specific resin for powder coatings is known for the field of powder coatings -- \*\*\*\* (publication number No. 25561 [ six to ]) -- the powder coatings which have antibacterial [ which used the zeolite particle which supported the metal in which antibacterial is shown ] were not known

[0005]

[Problem(s) to be Solved by the Invention] this invention tends to offer the polyester resin constituent for powder coatings which has antibacterial [ which can be comparatively manufactured by the low cost ], and a fungus resistance.

[0006]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, by blending the zeolite particle which made the polyester resin for powder coatings support a specific metal ion, this invention persons found out that the polyester resin constituent for powder coatings which has antibacterial and a fungus resistance was obtained, and completed this invention.

[0007] That is, this invention makes a summary antibacterial and the polyester resin constituent for fungus-resistance powder coatings which are characterized by blending the zeolite particle which made the metal ion chosen as the polyester resin for powder coatings whose limiting viscosity is 0.15 - 0.40 dl/g from silver, copper, and zinc support 0.01 to 10% of the weight.

[0008] Hereafter, this invention is explained in detail.

[0009] In this invention, the polyester resin for powder coatings requires that limiting viscosity should be the thing of 0.15 - 0.40 dl/g. When limiting viscosity is less than 0.15 dl/g, the blocking resistance of a constituent becomes bad, and on the other hand, when exceeding 0.40 dl/g, a

grindability becomes bad. The limiting viscosity of especially a desirable thing is the thing of 0.20 - 0.35 dl/g.

[0010] Furthermore, since it is an object for powder coatings, the thing of the range of softening temperature 50 - 150 °C is desirable.

[0011] The resin which softening temperature fine-particles-sized at less than 50 degrees C condenses, it is easy to solidify, and there is an inclination for a blocking resistance to be inferior. On the other hand, softening temperature If it exceeds 150 degrees C, kneading temperature must be made high, a part of reaction with a curing agent already progresses at the time of melting kneading, and there is an inclination for the smooth nature and the mechanical strength of a paint film to fall as a result.

[0012] A main end can use anything of a type for the polyester resin for powder coatings by this invention, although there are polyester resin of a hydroxyl and polyester resin of a carboxyl group.

[0013] When a main end is polyester resin of a hydroxyl, a hydroxyl value What is 230-1500geq / 106g is desirable. Big irregularity arises that hydroxyl values are less than 230geq(s)/106 on the surface of a paint film, and smooth nature falls. On the other hand, a paint will become expensive if it adds so that it may become the amount of functional groups corresponding to the hydroxyl value of a resin for about [ that the mechanical strength of a paint film falls ], and a curing agent if a hydroxyl value exceeds 1500geq(s) / 106g.

[0014] When a main end is polyester resin of a carboxyl group, the acid number What is 230-1500geq / 106g is desirable. The acid number Big irregularity arises that they are 230geq / less than 106g on the surface of a paint film, and smooth nature falls. On the other hand, if the acid number exceeds 1500geq(s) / 106g, the mechanical strength of a paint film will fall.

[0015] As an acid component of polyester resin, alicyclic group dicarboxylic acids, such as aliphatic dicarboxylic acids, such as aromatic dicarboxylic acids, such as a dicarboxylic acid, for example, a terephthalic acid, an isophthalic acid, and phthalic anhydride, an adipic acid, a sebacic acid, an azelaic acid, and dodecane 2 acid, and a cyclohexane dicarboxylic acid, are mainly used. You may use together the carboxylic acid more than trivalence, such as trimellitic acid, pyromellitic acid, and a trimesic acid, in the range which does not make polyester resin gel with a dicarboxylic acid.

[0016] As an alcoholic component, a glycol, for example, ethylene glycol, neopentyl glycol, a diethylene glycol, a propylene glycol, 1, 4-butanediol, 1, 6-hexandiol, 1, 4-cyclohexane dimethanol, the ethyleneoxide adduct of bisphenol A, etc. are mainly used. You may use together the polyols, a trimethylol propane, a glycerol, a pentaerythritol, etc., of three or more organic functions in the range which does not make polyester gel with a glycol.

[0017] Moreover, you may carry out the little combined use of the hydroxycarboxylic acid, such as 4-hydroxybenzoic acid and epsilon-caprolactone.

[0018] The polyester resin in this invention can be prepared by the conventional method of polyester manufacture by using the above components (those ester plasticity derivatives being included.) as a raw material.

[0019] In this invention, the zeolite particle which made the above polyester resin for powder coatings support a metal ion is blended. Since powder coatings mix a curing agent and various additives and carry out melting kneading in the manufacturing process, antibacterial and the antifungal agent to be used must not affect the reaction of polyester resin and a curing agent the top which needs a certain amount of thermal resistance. The zeolite particle which made the metal ion used by this invention support has agreed on this condition.

[0020] As for a metal ion, in the zeolite particle which made the metal ion used by this invention support, being supported by the ion exchange is desirable. It is not based on the ion exchange but there is a possibility that a problem may only produce metallic compounds in the sterilization effect and its durability in what adsorbed or adhered. As a metal ion, more than a kind of silver with sterilization nature, copper, and zinc is used.

[0021] In this invention, the zeolite particle which makes the metal ion chosen from silver, copper, and zinc support is an aluminosilicate. Many kinds from which a zeolite differs [ specific

surface area / the composition ratio and pore size, ] of things are known. However, specific surface area is more than 150m<sup>2</sup>/g (anhydrous zeolite criteria), and SiO<sub>2</sub> / aluminum<sub>2</sub>O<sub>3</sub> mole ratio of a zeolite constituent have [ 14 or less ] especially 11 or less thing desirable [ the zeolite particle used by this invention ]. It is possible to make the metal ion in which SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub> mole ratio has a germicidal action in 14 or less zeolite support uniformly, and sufficient sterilization effect is acquired by using such a zeolite.

[0022] As a zeolite material used by this invention, all of the zeolite of nature and composition are usable.

[0023] as a natural zeolite -- announcer RUSHIN (Analcime:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>= 3.6-5.6) A chavazite (Chabazite:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>= 3.2-6.0 and 6.4-7.6), Clinoptilolite (Clinoptilolite:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>= 8.5-10.5), Erionite (Erionite:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>= 5.8-7.4), Faujasite (Faujasite:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>= 4.2-4.6), A mordenite (Mordenite:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>=8.34-10.0), a FIRIPPU site (Phillipsite:SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>= 2.6-4.4), etc. are mentioned.

[0024] As permutite, A- type zeolite (SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>=1.4-2.4), X type zeolite (SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>=2-3), Y- type zeolite (SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>=3-6), a mordenite (SiO<sub>2</sub>/aluminum<sub>2</sub>O<sub>3</sub>=9-10), etc. are mentioned.

[0025] Especially desirable things are A- type zeolite, X type zeolite, Y- type zeolite, and a mordenite in a natural zeolite at a mordenite and a chavazite, and permutite.

[0026] Although what is necessary is for the configuration of a zeolite to have a desirable impalpable-powder-like thing and just to choose a particle diameter suitably if needed, it is 5 micrometers preferably. It is especially 2 micrometers hereafter. The following are suitable.

[0027] In the resin constituent of this invention, the rate for which an antibacterial zeolite particle accounts in a constituent needs to carry out to 0.01 - 10 % of the weight (as an anhydrous zeolite). The amount of an antibacterial zeolite particle is dissatisfied in respect of the sterilization effect at less than 0.01 % of the weight, and when it considers as a paint exceeding 10 % of the weight the top where the sterilization effect is almost eternal also as 50 % of the weight, mechanical physical properties become low.

[0028] The zeolite particle which made the metal ion support can be added to the polyester resin for powder coatings in the arbitrary stages at the time of composition of the polyester resin for powder coatings, or paint-izing.

[0029] When making the resin constituent of this invention into powder coatings, it is required to blend a curing agent.

[0030] When a main end uses the polyester resin of a hydroxyl, an isocyanate system curing agent, a glycoluril system curing agent, etc. are used. as an isocyanate system curing agent -- the Huels make -- B 1530, B 1065, and BF 1540 etc. -- it is mentioned as a glycoluril system curing agent -- POWDERLINK 1174 made from a tetramethoxy methyl glycoluril curing agent, for example, SAITEKKU, etc. -- it is mentioned the amount of functional groups almost corresponding to the amount of hydroxyl groups of polyester resin in the amount of the curing agent used -- desirable -- 0.8-1.2 Considering as the range of the twice equivalent is appropriate.

[0031] Moreover, when a main end uses the polyester resin of a carboxyl group, the EPI screw type epoxy resin guided from bisphenol A and epichlorohydrin, a melamine system curing agent, triglycidyl isocyanurate, etc. are used. as an EPI screw type epoxy resin -- \*\*\*\* Chemicals company make -- as YD-128, YD-014 grade, and a melamine system curing agent -- product made from Rohm&Haas As Primid XL-552 grade and triglycidyl isocyanurate, the Araldite PT 810 grade made from Ciba-Geigy is mentioned. the amount of functional groups almost corresponding to the acid number of polyester resin in the amount of the curing agent used -- desirable -- It is appropriate that it takes 0.8 to 1.2 times for the range of the equivalent.

[0032] In addition, the additive of pigments, such as a leveling agent, a curing catalyst, a titanium dioxide, and carbon black, and others can be blended if needed.

[0033]

[Function] Since the metal ion chosen as the zeolite from silver, copper, and zinc is held according to ionic bond, antibacterial [ excellent in the polyester resin constituent for powder

coatings of this invention ] and the reason for having a fungus resistance are safe, and are guessed for the effect to continue. Moreover, since the zeolite is excellent also in thermal resistance, it is imagined to be that from which antibacterial and the polyester resin constituent for powder coatings of a fungus resistance are comparatively obtained by the low cost satisfactory by a powder-coatings manufacturing process and the heat at the time of printing.

[0034]

[Example] Next, an example explains this invention. In addition, the measuring method of weighted solidity is as follows.

(a) Weight mixture, such as a limiting viscosity phenol and an ethane etc. tetrachloride, was used as the solvent, and it asked from the solution viscosity measured at 20 degrees C.

(b) After carrying out hydroxyl value acetylation, it titrated and asked with the potassium-hydroxide methanol solution.

(c) It dissolved in the acid-number dioxane, and titrated and asked with the potassium-hydroxide methanol solution.

(d) According to the specular gloss JIS K 5400, it asked 60 degrees.

(e) Apply to shock resistance JIS K 5400 correspondingly, and they are diameters 1/2. It asked using the inch and the 1kg sphere.

(f) on a phosphoric-acid zinc processing steel plate with an antibacterial diameter of 30mm, a paint constituent is painted so that a paint film may become uniform -- bake for 20 minutes at 190 degree C, and obtain a test piece Next, they are 1l. of water, and grape sugar about a test piece. 40g, peptone 10g, agar It sticks in the center of the cultivation side of plate agar which consists of composition of 10g. Further *Aspergillus niger*, *Penicillium funiculosum*, *Cladosporium cladosporioides*, and *Aureobasidium Pullulans* 1ml of mixed spore suspension is equally scattered the front face of a culture medium, and on a test piece, a Petri dish is covered, and it cultivates for 14 days at 28 degrees C. And the case where the case where a bacillus grows the case where a bacillus does not grow, or less [ of ++ and a test piece ] to 1/3 is grown to or more about +1 / 3 is shown as -.

[0035] Antimicrobial agent A-D used in the example shows the following.

[0036]

A: Complex ion. supported natural mordenite B: -- natural mordenite C: which supported the copper ion -- natural chavazite D: which supported the complex ion -- for an esterification reaction can in the amount (weight section) which showed the raw material compound shown in one to synthetic A- type zeolite examples 1-4 and example of comparison 3 table 1 which supported the complex ion in Table 1 2.5 kg/cm<sup>2</sup> Under pressurization By 160 - 250 \*\*, the esterification reaction was performed for 4 hours and the esterification object was prepared except for the water to generate out of the system of reaction. As [ after transporting the obtained esterification object to a polycondensation reaction can ] a catalyst. Antimony trioxide 5.83g (2x10<sup>-4</sup> mols /, acid component mol), triethyl phosphate 3.65g (2x10<sup>-4</sup> mols /, acid component mol), tetrabutyl titanate 0.68g (0.2x10<sup>-4</sup> mols /, acid component mol) was added, the polycondensation reaction was performed at the bottom of reduced pressure of 0.4hPa, and 280 degree C for 3 hours, and the polyester of limiting viscosity 0.45 dl/g was obtained. Subsequently, it added in the amount (weight section) which showed the compound indicated in this polyester at the column of the depolymerization of Table 1 in Table 1, and the depolymerization reaction was performed at the bottom of an ordinary pressure, and 270 degree C in the inert atmosphere for 1 hour, and the polyester resin which has the weighted solidity shown in Table 1 was obtained. It is blocked isocyanate system curing agent; Huels make to the obtained polyester resin. B 1530 The sum total of the amount of functional groups corresponding to the hydroxyl value of polyester resin, the becoming amount, a resin, and a curing agent As opposed to the 100 weight sections The amount (weight section), dioctyl tin maleate which showed the antimicrobial agent shown in Table 1 in Table 1 (curing catalyst) ; the Sankyo organic synthesis company make Stann OMF The 0.3 weight sections, butyl polyacrylate system leveling agent; -- the BASF A.G. make -- Acronal 4F -- 1 weight section -- benzoin the 0.5 weight sections and titanium-dioxide pigment; Ishihara Sangyo Kaisha, Ltd. make -- rutile-titanium-dioxide CR-90 50

weight sections come out comparatively and it adds. --46 after carrying out dryblend by the FM 10B type Henschel mixer (made in a Mitsui 3 pond factory) A type KO kneader (product made from Buss) is used. Melting kneading was carried out at 110 degrees C, the cooling and pulverization back and the wire gauze of 140 meshes separated, and powder coatings were obtained.

[0037] the obtained powder coatings are electrostatically painted on a phosphoric-acid zinc processing steel plate -- the 60-degree specular gloss of a paint film and shock-proof and antibacterial evaluation were performed about the test piece which performed printing for 20 minutes at 180 degree C The evaluation result of a paint film performance is shown in Table 1.

[0038]

[Table 1]

		実 施 例				比 較 例		
		1	2	3	4	1	2	3
原料	テレフタル酸	16600	16600	11620	16600	16600	11620	16600
	イソフタル酸	—	—	4980	—	—	4980	—
	エチレングリコール	4650	5580	8370	4030	5270	8060	4650
	ジエチレングリコール	—	—	—	1060	530	530	—
	ネオペンチルグリコール	6240	4680	—	6240	4680	—	6240
解重合	トリメチロールプロパン	402	—	670	894	—	804	—
	グリセリン	—	460	—	—	460	—	460
	ネオペンチルグリコール	—	—	—	—	—	—	208
極 限 粘 度 (dl/g)		0.35	0.26	0.22	0.18	0.24	0.21	0.19
水 酸 基 価 (eq/10 <sup>3</sup> g)		418	721	776	935	734	772	926
抗菌剤の種類		A	A	B	B	A	C	—
抗菌剤の添加量 (重量部)		1	5	2	5	0.001	20	—
60度鏡面光沢度 (%)		95	96	94	95	98	95	97
耐 衝 撃 性 (cm)		40	50	30	50	50	10	50
抗 菌 性		++	++	++	++	—	++	—

[0039] It tried to prepare powder coatings like an example 1 using the polyester resin of limiting viscosity 0.45 dl/g before the depolymerization reaction in example of comparison 4 example 1. Trituration of polyester resin was difficult and was not able to obtain the powder coatings with which an examination can be presented.

[0040] It used in the amount (weight section) which showed the raw material compound shown in five to example 7 table 2 in Table 2, and the polyester of limiting viscosity 0.45 dl/g was obtained like the example 1. Subsequently, it added in the amount (weight section) which showed the antimicrobial agent which showed the compound indicated in this polyester at the column of the depolymerization of Table 2 in the amount (weight section) shown in Table 2, and Table 2 in Table 2, and the depolymerization reaction was performed at the bottom of an ordinary pressure, and 270 degree C in the inert atmosphere for 1 hour, and the polyester resin which has the weighted solidity shown in Table 2 was obtained. The amount addition of said of the compound except an antimicrobial agent was carried out with the example 1 at the obtained polyester resin, and powder coatings were obtained like the example 1. Using the obtained powder coatings, a test piece is obtained like an example 1 and the result which evaluated the paint film performance is shown in Table 2.

[0041]

[Table 2]

		実 施 例		
		5	6	7
原 料 化 合 物	テレフタル酸	16600	16102	—
	イソフタル酸	—	—	15438
	アジピン酸	—	444	1036
	エチレングリコール	930	2170	2170
	ジェチレングリコール	12480	—	10400
	ネオペンチルグリコール	—	10400	—
解 重 合	トリメチロールプロパン	670	—	201
	グリセリン	—	230	—
	ネオペンチルグリコール	174	260	156
抗菌剤の種類		C	D	A
抗菌剤の添加量 (重量部)		100	200	200
極 限 粘 度 (dl/g)		0.20	0.23	0.32
水 酸 基 価 (seq/10 <sup>6</sup> g)		812	586	317
60度鏡面光沢度 (%)		96	98	95
耐 衝 撃 性 (cm)		30	30	30
抗 菌 性		++	++	++

[0042] It used in the amount (weight section) which showed the raw material compound shown in five to examples 8-11 and example of comparison 6 table 3 in Table 3, and the polyester of limiting viscosity 0.45 dl/g was obtained like the example 1. Subsequently, it added in the amount (weight section) which showed the compound indicated in this polyester at the column of the depolymerization of Table 3 in Table 3, and the depolymerization reaction was performed at the bottom of an ordinary pressure, and 250 degree C in the inert atmosphere for 3 hours, and the polyester resin which has the weighted solidity shown in Table 3 was obtained. Except having changed the curing agent and the curing catalyst into the obtained polyester resin as follows, the amount addition of said of the same compound as an example 1 was carried out with the example 1, and powder coatings were obtained like the example 1. Using the obtained powder coatings, a test piece is obtained like an example 1 and the result which evaluated the paint film performance is shown in Table 3.

Curing agent: EPI screw type epoxy resin;

\*\*\*\* Chemicals company make YD-128 (examples 8-9 and example 5 of comparison)

\*\*\*\* Chemicals company make YD-128 (examples 10-11 and example 6 of comparison)

Curing catalyst: 2-undecyl imidazole;

Cure ZORU by the Shikoku Chemicals company C11Z The 0.2 weight sections. [0043]

[Table 3]

		実 施 例				比 較 例	
		8	9	10	11	5	6
原 料 化 合 物	テレフタル酸	16600	8300	13280	16600	14900	16600
	イソフタル酸	—	8300	3320	—	—	—
	アジピン酸	—	—	—	—	1460	—
	エチレングリコール	2170	1860	5270	4650	3410	930
	ネオペンチルグリコール	10400	10920	5200	6240	8320	12480
解 重 合	トリメリット酸	630	840	420	1050	840	1050

合	イソフタル酸	—	—	830	830	332	—
極 限 粘 度	(dl/g)	0.28	0.22	0.21	0.16	0.23	0.25
酸 価	(geq/10 <sup>3</sup> g)	415	537	753	1178	611	658
抗菌剤の種類		C	D	A	B	—	D
抗菌剤の添加量	(重量部)	0.5	1	0.5	1	—	50
60度鏡面光沢度	(%)	93	96	97	94	97	86
耐 衝 撃 性	(cm)	50	30	40	50	50	10
抗 菌 性		++	++	++	++	-	++

[0044]

[Effect of the Invention] According to this invention, the polyester resin constituent for powder coatings which has antibacterial and a fungus resistance is comparatively offered by the low cost.

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[Translation done.]